A Study on the Durability of Selected Construction Metals in Acidic Conditions

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Hydrogen chloride (HCl) and sulphuric acid (H_2SO_4) are often formed when chlorine and sulphur containing volatile organic compounds (VOCs) are oxidised in catalytic incineration. Due to these acidic products, the durability of construction materials (e.g. SMO254, AISI316, Aluzinc) is one of the key issues in designing pilot and industrial scale incinerators. The potential problems caused by corrosion have to be eliminated or at least minimized. In this study, the effect of acidic process conditions on different metals and alloys were evaluated at a laboratory scale.

HCl and H_2SO_4 were used in the experiments in liquid phase and also as vapours. The liquid phase tests were performed in ambient conditions using three different acid concentrations. In gas phase tests, the starting concentrations of the acids were 10 vol-% for HCl and 20 vol-% for H_2SO_4. The analysis techniques used to evaluate the corrosion effects on metals were weighing, Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectrometry equipped with Attenuated Total Reflection unit (ATR-FTIR), and Atomic Absorption Spectrometry (AAS). In addition, visual observation confirmed by photos was used as well.

The results showed that in the experimental conditions studied HCl was always more corrosive compound than H_2SO_4. For the same time of exposure, higher corrosion rates were observed with gas phase tests than in liquid phase tests. The variation of acid concentration does not seem to fit many materials since they rarely persist both concentrated and diluted acids.

Keywords: VOC, Catalysis, Corrosion, HCl, H_2SO_4, Hastelloy, Titanium, Steel

1. Introduction

Catalytic oxidation, among others, has proven to be a feasible and affordable abatement technology of emissions of volatile organic compounds (VOC) originating from stationary sources. However, the use of catalytic oxidation to novel application areas, such as to the abatement of organic emissions containing sulfur (SVOC) and chlorine (CVOC), is not straightforward. (Ojala *et al.*, 2006) In catalytic oxidation VOC emissions are oxidized to CO_2 and H_2O, and in the case of CVOC or SVOC also to HCl and SO_2. As catalytic oxidation systems can produce secondary combustion wastes, halogens and sulphur compounds can be converted to their acidic species. (Everaert & Baeyens, 2004; Khan & Ghoshal, 2000) This poses a demanding task for the development of more selective catalysts, as well as construction materials of industrial abatement facilities.

One possible oxidation product in CVOC oxidation is Cl_2, a poisonous gas which can contact with many metals without harmful corrosion if the gas does not contain moisture. However, water formed as a product of oxidation of VOCs in catalytic incineration creates problems, since many metals are corroded by moist chlorine gas. Temperatures in catalytic combustion ranges between 300° and 650°C (Moretti, 2001; Ojala, 2005; Pitkäaho, 2006), and during shutdowns temperature in an incinerator can decrease to ambient temperature – even sub-zero during winter times. The concentration, different combinations of operating temperature, impurities and chemical stoichiometry of combustion reactions, combined with constructional features of the combustor design can lead to many possible corrosion reactions.

In this study, the impact of air and the effect of acidic conditions on different metals and alloys were evaluated in a laboratory scale. The corrosion behaviours of these selected metals were examined in different concentrations of HCl and H_2SO_4 in liquid and in vapour phase.

2. Experimental

Seven different potential construction materials for CVOC or SVOC catalytic oxidizers were studied. In addition, some steels were coated with special coating Ceracoat. Even under development, this composite was included in this study in order to preliminarily test its suitability in these conditions. The compositions and EN numbers of materials tested are listed in Table 1. For the experiments in liquid phase in ambient conditions, two acids, HCl and H_2SO_4 in three different concentrations and three different exposure times (one day, one week, two weeks) were used. The concentrations are presented in Table 2. After the metal pieces were cut and weighted, the metals were put into testing tubes, three pieces of each tube. Strong and diluted acids were poured slowly into the tubes (about 15 ml per tube). The tubes were left unclosed during the entire time of exposure since contact of air on the metal surface and acid was desired as it was one of the experimental parameters simulating real conditions in catalytic incinerator.

Table 1. Alloy compositions (wt-%)

EN	Alloy name	C	Cr	Ni	Mo	Fe	Others
1.4401	AISI316	0.02-0.04	17.2	10.1	2.1	Bal.	-
1.4547	SMO254	0.01	20	18	6.1	Bal.	0.7 Cu, 0.2 N
1.4539	904L	0.01	20	25	4.3	Bal.	1.5 Cu
1.4462	2205	0.02	22	5.7	3.1	Bal.	0.17 N
	Hastelloy C22	0.01	22	56	13	3.0	3 W, 2.5 Co, 0.35 V, 0.08 Si, 0.5 Mn
	Titanium (Ti11)						0.2 Pd
	AZ185 (Aluzinc)		Steel coated with Al (55%), Zn (43.4%), and Si (1.6%)				
	Ceracote-composite		Steels (CR.2, 304, 316) coated with Ceracoat$^{®}$ (composition not known)				

Table 2. Acid concentrations (vol-%)

Acid	Liquid tests			Vapor tests
HCl	37	20	4	10
H_2SO_4	95	20	4	20

For the experiment in gas phase, the concentration changed because the temperature used was high enough to evaporate water; and therefore, only one initial concentration of acids was tested (Table 2). As the acids were concentrated during the experiments increasing the boiling point of the mixture, the heating power was increased during the experiment. Acids were added periodically for four times during the test to attain the 6 hour exposure time. Vapour tests were done to simulate both the corrosion of hot acid gas and condensation of the gas on the metal surface.

By visual observation the analysis of corrosion was fast; changes in colour of the plates or solutions, presence of bubbles or salts, as well as colour of the precipitate, if there were any, could easily be observed. Weight measurements of the plates gave quantitative data. Analytical tools, Infrared Spectrometry equipped with Attenuated Total Reflection unit (ATR-FTIR) and Atomic Absorption Spectrometry (AAS) were used to find the compounds or the salts on the metal surfaces or solutions. The microstructures of the metal surfaces were pictured with Scanning Electron Microscope (SEM).

3. Results and discussion

The results showed in general that, in the experimental conditions studied, HCl was always a more corrosive compound than H_2SO_4.

3.1 Liquid phase tests

The colour of liquid was one possible way in determining if there was corrosion development or not. In addition to visual observation, weight change was followed as well. For example, visibly, the metals 254SMO, 2205, and 904L had exactly the same behaviour in diluted H_2SO_4 (20 vol-% and 4 vol-%): they did not react at all during 2 weeks. However, a slight change of weight was measured.

Table 3. AAS results with Hastelloy in HCl for 2 weeks (μg/l)

Concentration	Cr	Ni	Mo	Fe	Others
4vol-%	1823	8791	2808	20280	Co (9.6), V (26), Si (269), Mn (217)
37vol-%	449500	1340 000	336200	84760	Co (2832), V (2818), Si (1267), Mn (3357)

AAS was mainly used to identify the presence of metals in acids in the cases when visual observation of metal or colour of the solution did not show any signs of corrosion. AAS showed that even Hastelloy, the most resistant metal to HCl, dissolved to acid, more with strong 37vol-% than with weak 4vol-% acid (Table 3).

Some modifications of the structure of metals occurred at the micro-scale, which could not be observed with human eyes. In Figure 1 SEM pictures of every alloy are presented before and after 2 weeks of strong acid liquid phase tests. From these microstructures it can be seen how ‘fresh’ metals (Hastelloy, 254SMO, 904L and 2205) have homogeneous grains and as they are exposed to acids, they loose this microstructure indicating corrosion. SEM pictures confirmed the visual and weight measurements that the Hastelloy was the most durable metal in HCl solution.

After two weeks, the least resistant materials to HCl were Aluzinc and Ceracote, followed by 2205, 316, 904L, 254SMO, Titanium and Hastelloy, respectively. The least resistant materials to the solution of H_2SO_4 were Aluzinc, then 316, followed by 254SMO, 2205, 904L, and Titanium. For example, according to SEM and visual analyses 904 L did not react with H_2SO_4, but according to FTIR and AAS some corrosion existed. Aluzinc and Ceracote-composite lost their coatings in acids fast (in few hours), and since coated steels (CR.2, 304, 316) does not stand acids, they corroded fast. This loss of coating with Ceracote seemed to be due to the porosity of the coating. Coating was literally pealing of from the metal as it was exposed to liquid or gas phase acids.

3.2 Gas phase tests

By visual observations, the corrosion of metal plates in the gas phase was analyzed to be strong and it differed from the corrosion on a solid-liquid interface. During the vapour tests as the first droplet condenses on the surface of the metal, temperature is high. The first condensate has a high acid concentration as well. After 6 hours of testing, the least resistant materials to the fumes of HCl were Aluzinc and Ceracote followed by 2205, 316, 254SMO, 904L, Titanium and Hastelloy. The least resistant materials to the fumes of H_2SO_4 were Aluzinc and Ceracote followed by 316, 2205, 904L, and Titanium. Even though the time of exposure was shorter, the corrosion rate seemed to be increased compared to liquid phase tests. The higher temperature, the presence of moisture, and the changing concentration of the fumes (first 10 vol-%, then after evaporation of water, 20 vol-%, then at the end nearly 38vol-%) can explain this reactivity, even if the contact with the acids was less obvious (Kivisäkk, 2001).

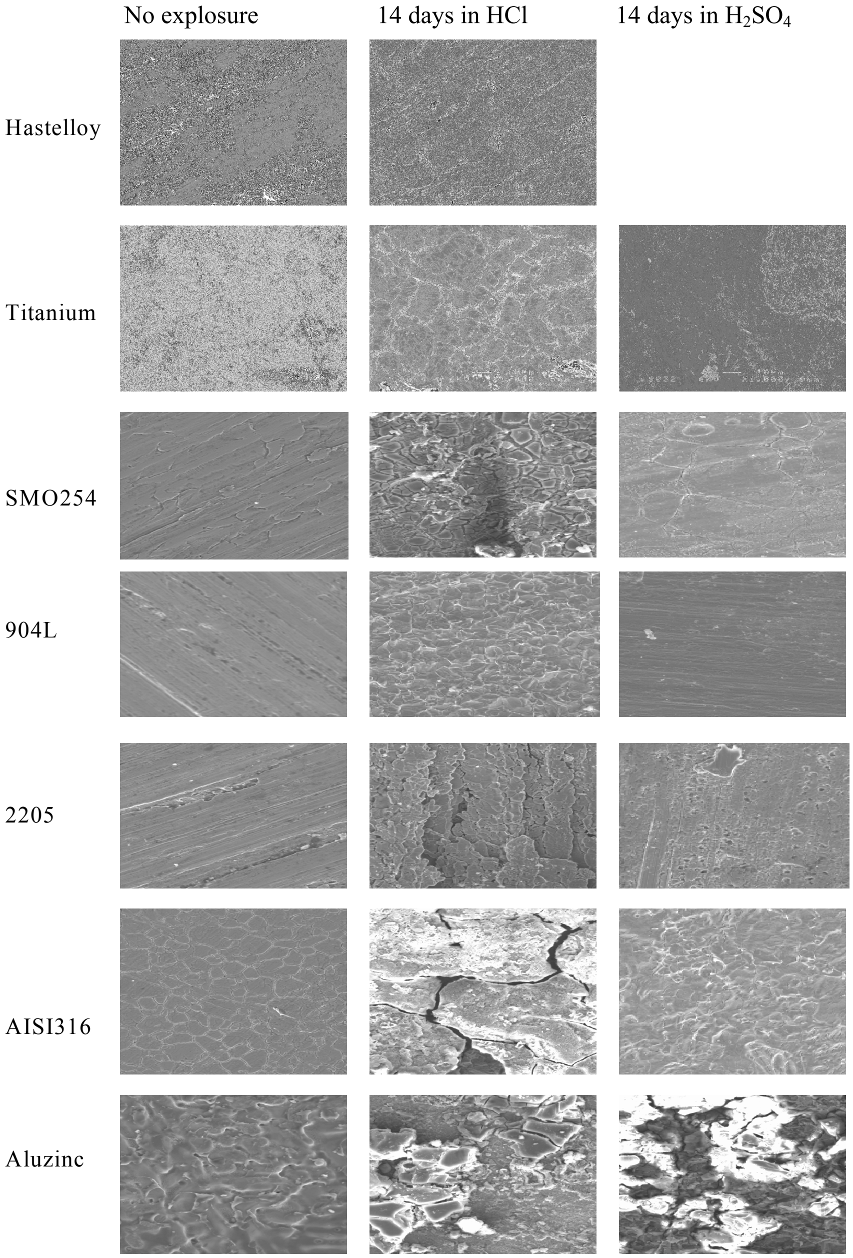

Figure 1. Metals without exposure and after 2 weeks in strong acids (37 vol-% HCl, 95 vol-% H_2SO_4) SEM, 1000x magnification.

4. Conclusions

In this study, the impact of air and the effect of acidic conditions on different construction metals and alloys were evaluated in a laboratory scale. The experiments were carried out imitating the real catalytic combustion conditions (the presence of moisture, changing concentration, and heat), in particular in the gas phase. The exposure time in liquid phase was two weeks, and even though it was quite short, it can bring ideas about the behaviour of a long duration exposure. The longer the exposure is, the more corroded the metals would be, but the first days are crucial in the evolution of the process. For the same time of exposure, higher corrosion rates were observed in gas phase tests than in liquid phase tests. The variation of acid concentration seems to be especially problematic to many materials since they rarely stand both concentrated and diluted acids. HCl was always more corrosive to the metals studied than H_2SO_4, it attacked each material in each condition according to the results of every analytical technique. Chloride ions are more able to pass through the passive layer and to dissolve metals than sulphate ions.

In our further study, different materials, especially new composite coating will be tested in order to find suitable and affordable construction materials for catalytic incinerator conditions.

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References

Everaert, K. & Baeyens, J, 2004, Catalytic combustion of volatile organic compounds. Journal of Hazardous Materials B109, pp. 113-139.

Khan, F.I. & Ghoshal, A.Kr. 2000. Removal of volatile organic compounds from polluted air. Journal of Loss Prevention in the Process Industries 13, pp. 527-545.

Kivisäkk, U. 2001. A test method for dewpoint corrosion of stainless steels in dilute hydrochloric acid, Corrosion Science 45, pp. 485–495.

Moretti, E.C. 2001. Practical solutions for reducing volatile organic compounds and hazardous air pollutants. USA, American Institute of Chemical Engineers (AIChE), 150 p. ISBN 0-8169-0831-1.

Ojala, S. 2005. Catalytic oxidation of volatile organic compounds and malodorous organic compounds. Dissertation. University of Oulu. Acta Universitatis Ouluensis Series C Technica 227, 135 p. ISBN 951-42-7869-0.

Ojala, S., Lassi, U., Härkönen, M., Maunula, T., Silvonen, R. & Keiski, R.L., 2006 Durability of VOC catalysts in solvent emission oxidation, Chem. Eng. Journal 120, pp.11-16

Pitkäaho, S. 2006. Catalytic incineration of volatile organic compounds, Master's thesis. University of Oulu, Department of Process and Environmental Engineering, 129 p.